ON A SUPPOSED ALLOTROPIC MODIFICATION OF PHOSPHORUS.

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In connection with Prof. Elihu Thomson, of the Artizan's Night School, the author has undertaken a series of experiments, resulting, it is believed, in the discovery of a new allotropic modification of phosphorus.

It is well known that when phosphorus is boiled in strong solution of potassium hydrate, and then allowed to cool slowly, it retains its liquid state for some time; but that if shaken, or touched with a sharp point it instantly solidifies.

We believe that in the cases heretofore observed, the property of retaining the liquid state is probably owing to the admixture with the ordinary phosphorus of an allotropic modification, having the property of retaining its liquid state indefinitely, and that, therefore, if this modification were obtained sufficiently pure, it would exhibit properties strikingly distinct from the common variety. We have undertaken the experiments, with the following results:

Good stick phosphorus is taken, and boiled for some time in strong solution of potassium hydrate, and water occasionally added to replace that lost by evaporation. Care must be exercised, by cautious stirring, to prevent the melted phosphorus from being carried to the surface by bubbles of disengaged gas. After boiling for five or ten minutes, the liquid phosphorus is carefully washed by replacing the alkaline solution by a stream of cold water. In this way the hypo-phosphates are removed, as well as the liquid and gaseous hydrides of phosphorus. The liquid modification thus obtained possesses the following peculiarities, which we believe entitle it to a place as one of the allotropic states of phosphorus:

1st. That of retaining for an apparently indefinite time its liquid condition, at temperatures far below the melting-point of the ordinary material. A carefully prepared specimen has been kept by us beneath a water surface for the past four months. It is still in the liquid state, at the time of making this communication and seems to promise to keep this state for an indefinite time. To make the retention of its liquidity still more striking, it may be remarked that the room in which the specimen is preserved has been for several weeks without a fire, the temperature probably reaching 40° F., a point far below the melting-point of ordinary phosphorus. The specimen in question was poured into a small test tube, and covered with about an inch of water. The test tube was then hung by a string in a place where it was secure from sudden jars or shaking. We have every reason for believing that this specimen, in common with numerous others experimented upon, will instantly solidify upon being touched.

A specimen of the liquid modification was placed beneath a water surface, and exposed to artificial cold produced by the evaporation of

ether. It solidified at about 38° F. With larger specimens and under more favorable conditions, the reduction may possibly be carried still further.

2d. Another peculiarity of the liquid modification is that of its non-oxidation when exposed to direct contact of air.

3d. As a result of this last mentioned property, the liquid does not shine in the dark. Ordinary and liquid phosphorus were exposed under the same circumstances to the air in a dark room. The common variety emitted the well known light, the other was entirely non-luminous.

There result apparently two distinct varieties of solid phosphorus from the solidification of the liquid modification. One is tough and waxy, like the ordinary material, the other is quite brittle and crystalline. We have noticed that in all cases well prepared specimens of the liquid produced on solidification the second variety, while poor or indifferent ones the first. We, therefore, regard that from which the second is produced as the true liquid modification.

The brittle crystalline solid thus produced comports itself somewhat differently from the ordinary variety. It oxidizes rapidly in the air, and raises its temperature so rapidly as to melt down into a liquid state, in which it is very easily inflammable.

In order to test whether the liquid modification underwent any change of volume at the moment of solidification, the following experiment was made: A small specimen was placed in a test tube, and covered with water. A stout glass tube, having one end drawn out into a capillary, was inserted into a cork, and tightly placed in the tube, The whole apparatus was then filled with water to within an inch of the top of the capillary. No appreciable change of volume could be detected at the moment of solidification, though it is possible that the diminution of bulk consequent on the passage from the liquid to the solid state, was exactly neutralized by the expansion produced through the heat developed by solidification.

To test whether the temperature of the boiling point had any effect in producing the liquid modification, stick phosphorus was boiled in a concentrated solution of zinc chloride. The result was a variety which with difficulty retained its liquidity, and on cooling, exhibited the waxy texture of the ordinary material. A high boiling point cannot, therefore, be the cause of the change.

Experiments were also made to ascertain whether the new modification were some compound of phosphorus with hydrogen. The result seemed to show this not to be the case. It may be mentioned incidentally, that during the conduct of some of these experiments a fact not generally known was observed. In a bulb blown in the middle of a glass tube small pieces of stick phosphorus were placed, and the ends of the tube were drawn out. One of these was placed in connection with a small hydrogen gasometer, and the phosphorus in the bulb melted by cautiously applied heat. Combination of course ensued, and there escaped from the free end of the tube a spontaneously inflammable hydride, whose tempera-

ture was so low as to render it incapable of igniting the free hydrogen issuing with it. After a few moments' heating, the tube was hermetically sealed. A liquid phosphorus was produced differing markedly from that obtained by boiling with caustic potash. It was very mobile, of a clear amber color, and on solidifying, assumed the tough, waxy state.

The physical peculiarities exhibited by the modification which we have studied seem fairly to entitle it to a place as one of the allotropic conditions of phosphorus. Indeed, they are much more strongly marked than those upon which the elastic variety of sulphur are based.

ABSTRACT OF THE REMARKS OF PROF. COPE AT THE MEETING OF THE AMERICAN PHILOSOPHICAL SOCIETY, JANUARY 16, 1874.

An analysis of the osteotology of the extinct ruminant *Poëbrotherium* (Leidy), from the Miocene of the Western territories, determines some interesting relations to the living and extinct members of the order. The cervical vertebræ indicate affinity to the *Camelidæ*, and there is nothing in the remainder of the structure to contradict such relation. The separation of the *os trapezoides* is found in the camels, and very few others only among *Ruminantia*, but in the presence of the *trapezium*, *Poëbrotherium* shows relationships to more ancient types, as *Anoplotheriidæ*, &c. The reduction of the digits to two, and the separation of the metacarpals, point in the same direction; indeed, the number of carpals and metacarpals is precisely as in *Xiphodon*. But the mutual relations of these bones are quite different from what exists in that genus, and is rather that of the *Camelidæ* and other Ruminants, or what Kowalevsky has called the "adaptive type." This author has seen in the genus *Gelocus*, Aym., from the lowest Miocene or upper Eocene the ancestor of a number of the types of the order, but among these he does not include the *Camelidæ*. The present genus is a more generalized type than *Gelocus*, in its separate trapezoid and distinct metacarpals, and represents an early stage in the developmental history of that genus. It also presents affinity to an earlier type than the *Tragulidæ*, which sometimes have the divided metacarpals, but the trapezoides and magnum co-ossified. In fact, *Poëbrotherium* as direct ancestor of the camels, indicates that the existing *Ruminantia* were derived from three lines, represented by the genera *Gelocus* for the typical forms, *Poëbrotherium* for the camels, and *Hyaemoschus* for the *Tragulidæ*. The first of these genera cannot have been derived from the second, on account of the cameloid cervical vertebræ of the latter, and all three must be traced to the source whence were derived also the *Anoplotheriidæ*, perhaps the little known *Dichodontidæ*.

The two distinct metacarpals, separate trapezium and trapezoides, cameloid cervical vertebræ, and dentition characterize this type as a peculiar family, which may be called *Poëbrotheriidæ*. The genus from which it takes its name was originally referred by Leidy to the *Camelidæ*. The genera *Hypertragulus*, Cope; *Leptomeryx*, Leidy; and *Hypisodus* Cope, are probably *Tragulidæ*.